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Light Harvesting and Efficient Energy Transfer in Dendritic Systems: New Strategy for Functionalized Near-Infrared BF_2-Azadipyrromethenes

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Abstract: A series of dendritic systems, which are capable of funneling energy from the periphery to the core, have been synthesized. The photophysical properties of the dendrimers, generations 0–2, have been determined. The light-harvesting ability of these compounds increases with increasing generation arising from the increase in molar extinction coefficient. Selective excitation of the donor leads to an efficient energy transfer (>90%) to the acceptor. The approach provides a facile synthesis for modification of near-infrared BF_2-Azadipyrromethene.

Keywords: chromophores · dendrimers · FRET · near-infrared · time-resolved spectroscopy

Introduction

In recent years, there has been considerable interest in the development of organic chromophores with spectral properties in the near-infrared (NIR) region as well as their applications in imaging in vitro and in vivo.[1] The advantages of imaging in the NIR region (650–900 nm) are numerous, and have been extensively discussed. Prominent among these advantages is the absence or significant reduction of background absorption, fluorescence, and light scattering.[2] Unfortunately, there are still many key problems encountered from the synthesis of NIR chromophores, such as spectral broadening, photobleaching, aggregation, photo-instability, and low quantum yields.[3] The most widely used NIR chromophores are the cyanines as well as a few other chromophores that are commercially available.[4] As such, the development of new NIR chromophores with high quantum yields remains a challenge.

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The aza-dipyrromethene (Aza-Bodipy) was first reported over 60 years ago[5] but remained unstudied until the pioneering work by O'Shea and co-workers.[6] Recently, Aza-Bodipy and related structural analogues have been reported as a new class of chromophore with high absorption extinction coefficients (70000–80000 $M^{-1}cm^{-1}$) and fluorescence quantum yields between 650–750 nm.[7] The photophysical characteristics suggest that this structural class would be an excellent platform for developing new NIR materials for numerous applications. Recently, much attention has been devoted to improving the photophysical properties of Aza-Bodipy. One major approach for optimizing the materials structure and to increase the emission efficiencies of Aza-Bodipy has recently emerged. This approach involves the preparation of constrained systems,[8] which has thus far produced NIR systems with enhanced quantum yields[9] that can be exploited for potential applications in photodynamic therapy[10] and as fluorescent chemosensors.[11]

Dendrimers, which consist of peripheral units, a core, and intervening branching units, are interesting scaffolds for light-harvesting applications (Figure 1). The periphery of the dendrimers functionalized with light-absorbing chromophores may funnel energy to a lower energy acceptor at the core. The increasing numbers of functionalities from the core to the periphery promise excellent candidates for light-harvesting antenna. The use of dendrimers for harvesting light has been elegantly demonstrated by several groups.[12] A new strategy promising simple and efficient modification to enhance the quantum yields of Aza-Bodipy is very urgent in both fundamental research and application. Recently, attention has focused on framework modification. However,

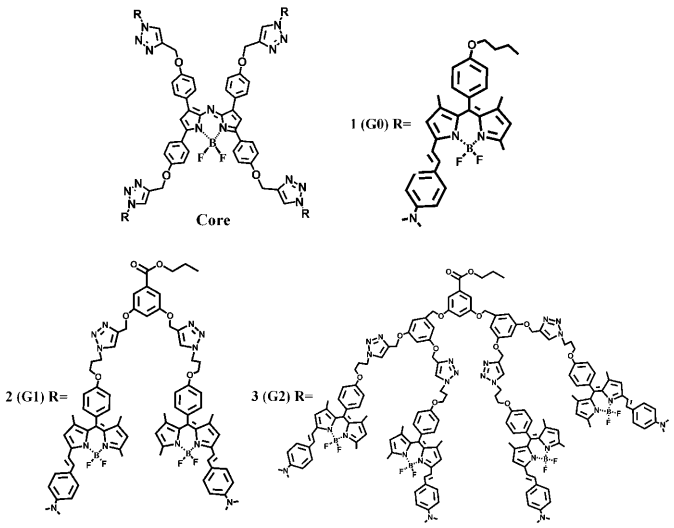

Figure 1. Structure of the dendritic light-harvesting systems (G0-G2).

utilizing dendrimers as light-harvesting antennae based on an Aza-Bodipy platform has never been reported.

Here, we present a new approach in which the multi-donor BODIPY chromophores are attached to a central Aza-Bodipy acceptor by efficient Cu^{I}-catalyzed 1,3-dipolar cycloaddition.[13,14] Appended antenna molecules transfer their excited-state energy to the core by fluorescence resonance energy transfer (FRET), and amplified emission is observed. The system displays efficient FRET and significant antenna effects on excitation with UV radiation.

Results and Discussion

Synthesis of the Aza-Bodipy core started with the diaryl α,β-unsaturated ketone **7** (chalcone), which was prepared by an aldol/dehydration reaction of the corresponding benzaldehyde and acetophenone derivatives (Scheme 1). Thus, Michael addition of nitromethane to the α,β-unsaturated ketone, with diethylamine (DEA) as base, gave the 1,3-diaryl-4-nitrobutanone **8** in quantitative yields. Condensation of **8** with ammonium acetate in ethanol under reflux for 24 h gave a moderate yield of azadipyrromethenes **9**. Complexation of azadipyrromethenes with $BF_3{\cdot}OEt_2$ gave the Aza-Bodipy **10** in high yields. The antenna section was synthesized starting from 4-(3-bromopropoxy)benzaldehyde. The aldehyde was then used in the usual manner in the synthesis of a BODIPY dye **4**. The reaction of **4** with NaN_3 in polar aprotic solvents gave compound **5** in nearly quantitative yields. Then, **5** reacted with *N*,*N*-dimethyl-4-aminobenzaldehyde and gave **6** in moderate yields.[15] The synthesis of the dendritic structure began with compounds **11** (generation 1) and **15** (generation 2), which have previously been reported.[26] To functionalize the dendrimers simply and efficiently, "click chemistry" was introduced to the reaction. In the presence of Cu^{I}, **6** reacted with **12** and **16** to yield BODIPY functionalized dendrimers **13** and **17**, respectively. Then, we treated dendrimers **13** and **17** with NaN_3 in DMF resulting in the azido-functionalized dendrimers **14** and **18** in high yield. Finally, a second "click chemistry" was conducted to yield the target light-harvesting systems. The azido-functionalized dendrimers (**14** and **18**) and the alkyne-functionalized Aza-Bodipy reacted together in the presence of $CuSO_4$ and sodium ascorbate at RT giving compounds **1**, **2**, and **3** in high yields. All new compounds were characterized by ^{1}H and ^{13}C NMR spectroscopy, and mass spectrometry.

Abstract in Chinese:

设计合成了一系列以氮杂氟硼二吡咯甲烷为核心的枝状化合物，并研究了它们的光物理和电化学性质。研究表明该体系显现出极强的光收集能力，外围到核心的能量转移效率在90%以上。随着代数的增加，氮杂氟硼二吡咯甲烷的量子产率得到了显著增长。本文为改善氮杂氟硼二吡咯甲烷的发光效率提出了一种简便有效的新方法。

The primary condition for energy transfer is the spectral overlap between the donor emission and the acceptor absorption.[16] This overlap is clear in Figure 2, in which the

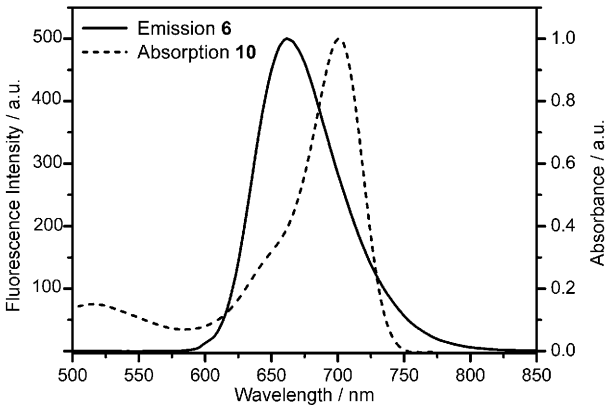

Figure 2. Emission spectrum of donor **6** and the absorption spectrum of **10**, both of them were measured in THF.

emission spectrum of **6** (with an excitation wavelength at 602 nm) and absorption spectrum of **10** are depicted. From this figure, it can be seen that the overlap of the donor emission and the acceptor absorption is extremely large. The large spectral overlap between the two interacting chromophores indicates that the possibility of donor–acceptor energy transfer should be high.

The UV/Vis absorption spectra of the dendritic series 1–3 in THF solution are shown in Figure 3a, and the absorption maxima (λ_{max}) and the extinction coefficient (ε) are collected in Table 1. As can be seen from the spectra, there are two distinct absorption bands, one is in the region 550–650 nm and the other is in the region 650–750 nm. The absorption in the region 550–650 nm is assigned to the donor chromophore.[17] The absorption maximum around 702 nm is attributed to the Aza-Bodipy chromophore. Comparison of the

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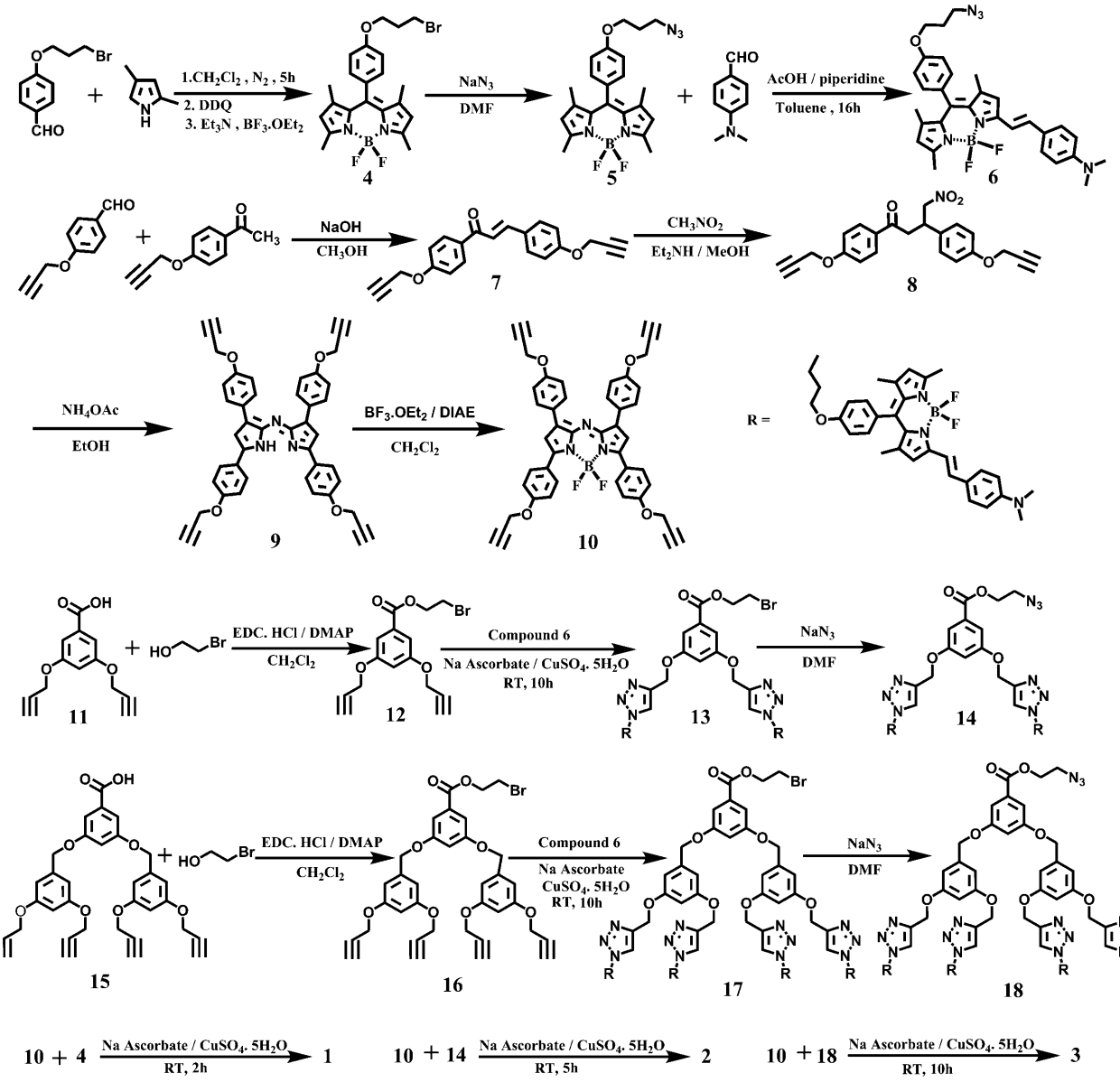

Scheme 1.

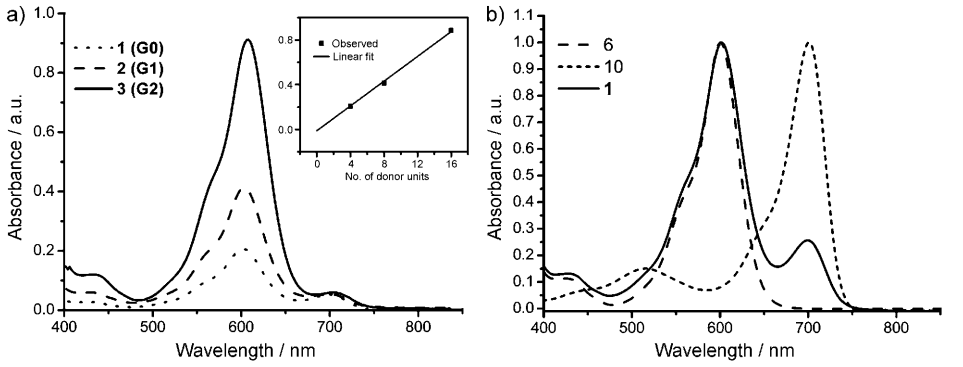

Figure 3. a) Comparison of the absorption spectrum of compounds **1**–**3**. The spectrum is normalized at the longer-wavelength peak that corresponds to the core. Inset: Plot of the number of donors in the dendrimers versus absorbance at 602 nm. b) UV/Vis spectra of donor **6**, acceptor **10**, and compound **1**, recorded in THF solution and normalized at 602 nm.

absorption spectra of the dendrimers G0, G1, and G2 (**1**, **2**, **3**) shows that the molar extinction coefficient and the position of the longer band remained constant. The absorption in the region 550–650 nm of these compounds increases steadily with increasing generation. This is attributed to the increasing number of the donor units with increasing generation. Also, it should be noted that there is no spectral broadening or spectral shift

Table 1. Values of λ_{max} and ε for the dendritic compounds in THF.

Compd	λ_{max} (abs) [nm]	ε [$M^{-1}cm^{-1}$]	λ_{max} (abs) [nm]	ε [$M^{-1}cm^{-1}$]
6	602	8.9×10^4		
10	702	8.7×10^4		
1	602	3.52×10^5	702	8.7×10^4
2	602	7.13×10^5	703	8.8×10^4
3	602	1.41×10^6	703	8.7×10^4

with increasing generation. As shown in Figure 3b, the steady-state absorption spectrum of compound **1** is quite similar to the sum of the absorption spectra of the component chromophores. Similar behavior is also observed for **2** and **3**. This provides evidence for the lack of direct electronic communication between the BODIPY antenna and the Aza-Bodipy core in the electronic ground state.[18]

FRET between the donor and the acceptor was confirmed using fluorescence measurements of **1**, **2**, **3**, **6**, and **10**. Excitation of the dendritic compounds **1**, **2**, and **3** at 602 nm (the donor absorption maximum) resulted in an emission predominantly from the acceptor dye at about 735 nm. The emission spectra shows almost complete quenching of the donor emission at 650 nm when **1**, **2**, and **3** are excited at 602 nm. For example in Figure 4, when excited at 602 nm, **1** showed a ~1.3-fold ($\Phi = 0.21$) increase in acceptor emission, relative to the direct excitation of acceptor at 702 nm ($\Phi = 0.16$). This significant 'antenna effect' indicates that energy-transfer efficiency is extremely high in this molecule. As the donor units increases with increasing generation, the 'antenna effect' exhibits more clearly. On the other hand, **2** (generation 1) showed a ~2.4-fold ($\Phi = 0.38$) increase in acceptor emission, relative to the direct excitation of the acceptor and, **3** (generation 2) showed a larger increment of about 4.1-fold to produce a quantum yield about 0.66. Steady-state photophysical measurements of **1**, **2**, **3**, **6**, and **10** in THF enabled the determination of the approximate FRET efficiencies. The donor to acceptor FRET efficiencies were calculated by comparing the integrated donor emission in the presence of the acceptor, relative to the donor emission in the absence of the acceptor.[19] Donor BODIPY emission in **1** is quenched by 93% relative to its emission in compound **4**. So, the study resulted in calculated FRET efficiencies of 93% from donor to acceptor. Similar studies using **2** and **3** resulted in calculated FRET efficiencies of 90% and 86%, respectively.

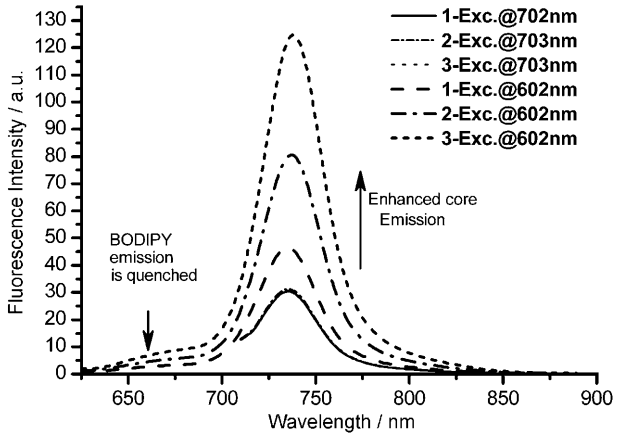

Figure 4. Enhanced core emission on excitation of the donor BODIPY units in dendritic molecules **1**, **2**, and **3**.

To further confirm the energy transfer from the BODIPY antenna to the central Aza-Bodipy, a time-resolved fluorescence experiment was conducted. Time-resolved fluorescence measurements examine the fluorescence decay profile at different wavelengths and can provide evidence of interrelated processes, such as energy transfer. Fluorescence decays for all compounds were carried out in THF solution using the time-correlated single-photon-counting method. The sample was excited at 602 nm, and the fluorescence decay was monitored at the emission maximums: 650 nm for the donor compound **6** and 735 nm for the acceptor compound **10**. In **1**, **2**, and **3**, emission at 650 nm was also monitored to determine the detection of the residue decay from the donor dyes. The data were fitted using a reconvolution method of the instrument response function (IRF) producing χ^2 fitting values of 1–1.5. The entire set of acquired data from the fluorescence decay experiment is summarized in Table 2.

Table 2. Summarized quantum yields, fluorescence maxima (Fl_{max}), and fluorescence lifetimes in THF.

	Fl_{max} [nm]	τ_{S1} [ns]	α_1	τ_{S2} [ns]	α_2	Fl_{max} [nm]	τ_{S3} [ns]	Φ
1	650	0.27	0.903	3.10	0.072	735	1.94	0.21
2	650	0.31	0.925	3.13	0.056	735	1.76	0.38
3	650	0.33	0.898	3.15	0.092	735	1.98	0.66
6	650	–		3.31		–	–	0.55
10	–	–		–		735	1.62	0.16

τ_{S1} and τ_{S2} refer to short-lived and long-lived emission, respectively. α_1 and α_2 are the contributions of each component to the total fluorescence intensity.

In compound **1**, the emission at 650 nm, corresponding to the donor BODIPY, exhibits a short component followed by a long-lived decay. The Aza-Bodipy emission at 735 nm exhibits a long-lived monoexponential decay. We assume that the short component is caused by energy transfer from the BODIPY antenna to the Aza-Bodipy core.[20] Thus, the emission at 650 nm yields biexponential lifetimes of 0.27 ns (τ_{S1}) and 3.10 ns (τ_{S2}), and then the emission at 735 nm has a lifetime of 1.94 ns (τ_{S3}). These lifetimes closely match those observed for the donor **6** (3.31 ns) and acceptor **10** (1.62 ns). When time-resolved fluorescence data are used, the calculated FRET efficiency for **1** is 91.8%. Similar calculations using the parameters extracted from our time-resolved data were performed. We obtain FRET efficiencies of 90.6% and 90% for G1 and G2, respectively (see Supporting Information). As can be seen from the calculated values, a discrepancy exists between the energy-transfer efficiencies from steady-state versus time-resolved data. These results show that the energy transfer from the periphery to the core is

the only pathway.[21] The proposed FRET process is shown in Figure 5. It is observed that with an increasing number of donors, the core's fluorescence increases steadily.

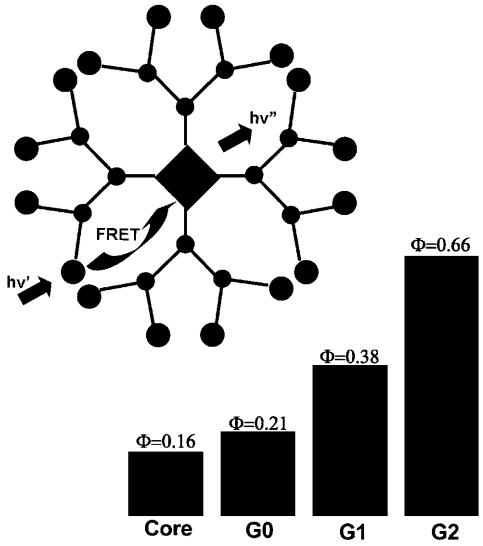

Figure 5. Proposed FRET process occurred in dendrimers **1**, **2**, **3**, and their quantum yields.

Conclusions

In conclusion, we have successfully demonstrated a new strategy for modifying Aza-Bodipy. A series of dendritic Bodipy antennae are efficiently attached to a central Aza-Bodipy core by "click chemistry". Selective excitation of the donor leads to a highly efficient energy transfer (>90%) to the acceptor, resulting in an enhanced acceptor emission. The synthesis process is a facile approach for extending the functionalization of the Aza-Bodipy to develop novel NIR dyes for numerous applications in optical devices.

Experimental Section

General

Unless otherwise stated, reagents were commercially obtained and used without further purification. 4-(3-bromopropoxy)benzaldehyde, 4-(2-propynyloxy)benzaldehyde,[24] 1-[4-(2-propynyloxy)phenyl]-1-ethanone,[25] 3,5-bis(2-propynyloxy)benzoic acid, 3,5-bis(3,5-bis(2-propynyloxy)benzyloxy)benzoic acid[26] were prepared according to literature.

Syntheses

4,4-Difluoro-8-(4-(3-bromopropoxy))phenyl-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene (4): 4-(3-bromopropoxy)benzaldehyde (242 mg, 1 mmol) and 2,4-dimethylpyrrole (190.3 mg, 2 mmol) were dissolved in CH_2Cl_2 (200 mL) under N_2 atmosphere. One drop of trifluoroacetic acid was added, and the light-red solution was stirred at room temperature for 5 h. A solution of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (227 mg, 1 mmol) in anhydrous CH_2Cl_2 (25 mL) was added by syringe, and the resulting mixture was stirred for 15 min followed by the addition of 4 mL triethylamine and 4 mL $BF_3{\cdot}Et_2O$. After stirring for another 30 min, the reaction mixture was washed with water (4×50 mL), and the organic phase was dried over Na_2SO_4. After concentration in vacuum, the residue was purified by column chromatography (silica gel, $CHCl_3$) to afford orange needles (166 mg, 36%). ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.18 (d, 2H), 7.01 (d, 2H), 5.98 (s, 1H), 4.16 (t, 2H), 3.64 (t, 2H), 2.55 (s, 6H), 2.36 (m, 2H), 1.44 ppm (s, 6H); ^{13}C NMR: δ=159.4, 155.4, 143.3, 141.9, 131.9, 129.4, 127.4, 121.3, 115.3, 69.0, 65.6, 32.5, 30.0, 14.7 ppm; MS (EI): *m/z* (%) calcd for $C_{22}H_{24}BBrF_2N_2O$: 460.1; found: 460.0; elemental analysis: calcd (%) for $C_{22}H_{24}BBrF_2N_2O$: C 57.30, H 5.25, N 6.07; found: C 57.48, H 5.01, N 6.38.

4,4-Difluoro-8-(4-(3-azidopropoxy))phenyl-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene (5): Dry DMF (3 mL) was added to a 10 mL-capacity flask containing compound **4** (230 mg, 0.5 mmol) and sodium azide (65 mg, 1 mmol). The mixture was stirred at RT for 4 h before being cooled. After the reaction was completed, the mixture was poured into water (50 mL), then extracted with $CHCl_3$ several times. The combined organic phase was dried over Na_2SO_4, and the solvent was removed under vacuum. The crude residue was purified by silica gel chromatography with CH_2Cl_2 as eluant, to afford an orange-red solid (191 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.18 (d, 2H), 6.99 (d, 2H), 5.97 (s, 1H), 4.11 (t, 2H), 3.56 (t, 2H), 2.55 (s, 6H), 2.10 (m, 2H), 1.43 ppm (s, 6H); ^{13}C NMR: δ=159.4, 155.4, 143.3, 141.9, 131.9, 129.4, 127.4, 121.2, 115.2, 64.8, 48.3, 28.9, 14.7 ppm; MS (EI): *m/z* (%)calcd for $C_{22}H_{24}BF_2N_5O$: 423.3; found: 423.0; elemental analysis: calcd (%) for $C_{22}H_{24}BF_2N_5O$: C 62.43, H 5.72, N 16.55; found: C 62.71, H 5.41, N 16.98.

3-{2′-(4″-dimethylaminophenyl)ethenyl}-4,4′-difluoro-8-(4-(3-azidopropoxy))-phenyl-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene (6): Compound **5** (460 mg, 1.1 mmol) and dimethylaminobenzaldehyde (180 mg, 1.2 mmol) were refluxed in a mixture of toluene (20 mL), piperidine (900 μl), glacial acetic acid (750 μl), and a small amount of $Mg(ClO_4)_2$. Any water formed during the reaction was removed azeotropically by heating overnight in a Dean–Stark apparatus. The solvent was removed under vacuum, and the residue was purified by silica gel column chromatography (CH_2Cl_2 to CH_2Cl_2/MeOH=100:1). The blue fraction was collected to afford a purple solid (256 mg, 42%). ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.51 (d, 2H), 7.48 (s, 1H), 7.23 (d, 1H), 7.18 (d, 2H), 7.00 (d, 2H), 6.59 (s, 1H), 5.96 (s, 1H), 4.11 (t, 2H), 3.56 (t, 2H), 3.00 (s, 6H), 2.59 (s, 3H), 2.10 (m, 2H), 1.47 (s, 3H), 1.43 ppm (s, 3H); ^{13}C NMR: δ=159.3, 154.8, 152.9, 151.2, 143.0, 140.9, 139.0, 137.8, 133.6, 131.7, 129.8, 129.3, 127.9, 124.8, 120.5, 117.7, 115.0, 114.6, 112.2, 64.8, 48.4, 40.3, 28.9, 15.0, 14.7, 14.6 ppm; MS (EI): *m/z* (%) calcd for $C_{31}H_{33}BF_2N_6O$: 554.4; found: 554; elemental analysis: calcd (%) for $C_{31}H_{33}BF_2N_6O$: C 67.15, H 6.00, N 15.16; found: C 67.42, H 6.03, N 14.94.

1,3-Di[4-(2-Propynyloxy) phenyl]propenone (7): A solution of 4-(2-propynyloxy)benzaldehyde (3.2 g, 20 mol) and 1-[4-(2-propynyloxy)phenyl]-1-ethanone (3.48 g, 20 mol) in absolute methanol (20 mL) was prepared either in a closed system or under nitrogen at RT. Catalytic amount of solid sodium hydroxide was added and the mixture was vigorously stirred at RT for 10 h. After the reaction was completed, the precipitate was filtered, washed with cold ethanol and water, and dried under vacuum to afford a white solid (5.7 g, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.03 (d, 2H), 7.77 (d, 1H), 7.60 (d, 2H), 7.42 (d, 1H), 7.05 (d, 2H), 7.00 (d, 2H), 4.76 (d, 2H), 4.73 (d, 2H), 2.56 ppm (m, 2H); ^{13}C NMR: δ=188.9, 161.3, 159.6, 144.0, 132.3, 130.9, 130.3, 128.8, 120.2, 115.5, 114.9, 78.3, 18.1, 76.4, 76.2, 56.1 ppm; MS (EI): *m/z* (%) calcd for $C_{21}H_{16}O_3$: 316.3; found: 316.0; elemental analysis: calcd (%) for $C_{21}H_{16}O_3$: C 79.73, H 5.10; found: C 77.46, H 5.31.

3-[4-(2-Propynyloxy)phenyl]-4-nitro-1-[4-(2-propynyloxy)phenyl]-butan-1-one (8): To the solution of 1,3-di[4-(2-propynyloxy) phenyl]-propenone **7** (390 mg, 1.2 mmol) in methanol (30 mL) was added diethylamine (6 mmol, 600 μL) and nitromethane (6 mmol, 400 μL). The mixture was then heated under reflux for 24 h. The solution was cooled and evaporated to dryness under vacuum. The residue was purified by silica gel chromatography with CH_2Cl_2/petrol ether (1:1) as eluant to afford a yellow powder (398 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.91 (d, 2H), 7.20 (d, 2H), 7.05 (d, 2H), 6.92 (d, 2H), 4.80 (m, 1H), 4.75 (d, 2H), 4.62 (d, 2H), 4.60 (m,1H), 4.17 (t, 1H), 3.40 (t, 2H), 2.55 (s, 1H), 2.51 ppm (s, 1H); ^{13}C NMR: δ=195.6, 161.8, 157.3, 144.0, 132.3, 130.9, 130.5, 130.3,

128.8, 115.6, 115.0, 80.0, 78.6, 76.2, 75.9, 56.1, 41.5, 38.9 ppm; MS (EI): *m/z* (%) calcd for $C_{22}H_{19}NO_5$: 377.4; found: 377.

{3,5-Di[4-(2-propynyloxy)phenyl]-1 H-pyrrol-2-yl}{3,5-di[4-(2-propynyloxy)-phenyl]pyrrol-2-ylidene}amine (9): A solution of 3-[4-(2-propynyloxy)phenyl]-4-nitro-1-[4-(2-propynyloxy) phenyl]-butan-1-one **8** (750 mg, 2 mmol) in THF (1 mL) was placed in a 50 mL-capacity flask, then ammonium acetate (12 g, 0.156 mol) was added. The mixture was dissolved in ethanol (20 mL) and heated under reflux for 24 h. The reaction solution was cooled to RT, and the solvent was concentrated to 10 mL, and filtered. The isolated solid was washed with large amount of methanol for several times. The residue was dried under vacuum to afford a brown solid (466 mg, 70%). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 8.32 (s, 1H), 8.06 (m, 8H), 7.53 (s, 2H), 7.25 (d, 4H), 7.12 (d, 4H), 4.96 (s, 4H), 4.91 (s, 4H), 3.66 (s, 2H), 3.61 ppm (s, 2H); ^{13}C NMR: δ = compound was too insoluble to record a spectrum; MS (MALDI): *m/z* (%) calcd for $C_{44}H_{31}N_3O_4$: 665.7; found: 665.6; elemental analysis: calcd (%) for $C_{44}H_{31}N_3O_4$: C 79.38, H 4.69, N 6.31; found: C 79.21, H 4.87, N 6.52.

BF_2 chelate of {3,5-di[4-(2-propynyloxy)phenyl]-1H-pyrrol-2-yl} {3,5-di[4-(2-propynyloxy)-phenyl]pyrrol-2-ylidene}amine (10): Compound **9** (666 mg, 1 mmol) was dissolved in dry CH_2Cl_2 (100 mL), treated with diisopropylethylamine (1.2 mL, 7 mmol) and $BF_3{\cdot}OEt_2$ (1 mL, 8 mmol), and stirred at RT for 10 h. The mixture was washed with water, and the organic phase was dried over sodium sulfate and evaporated to dryness. The residue was purified by silica gel chromatography with CH_2Cl_2/petrol ether (1:1) as eluant to afford a brown solid (571 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05 (m, 8H), 7.07 (m, 8H), 6.95 (s, 2H), 4.78 (d, 4H), 4.76 (d, 4H), 2.59 (s, 2H), 2.56 ppm (s, 2H); ^{13}C NMR ([D$_6$]DMSO): δ = 160.2, 159.2, 157.7, 145.0, 142.5, 132.1, 131.2, 125.8, 124.7, 118.9, 115.8, 115.7 ppm; MS (MALDI): *m/z* (%) calcd for $C_{44}H_{30}BF_2N_3O_4$: 713.5; found: 713.5; elemental analysis: calcd (%) for $C_{44}H_{30}BF_2N_3O_4$: C 74.06, H 4.24, N 5.89; found: C 74.43, H 3.93, N 6.22.

2-Bromoethyl-3,5-bis(2-propynyloxy)benzoate (12): To a stirred solution of 3,5-bis(2-propynyloxy)benzoic acid (230 mg, 1 mmol) and 2-bromoethanol (124 mg, 1 mmol) in anhydrous CH_2Cl_2 (50 mL) cooled on an ice bath, was added 4-DMAP (25 mg, 0.2 mmol) and EDC·HCl (205 mg, 1.1 mmol), and the reaction was allowed to stir for 10 h at RT. The solution was washed with a saturated solution of citric acid and H_2O. The organic layer was dried over anhydrous $MgSO_4$, and the filtrate was reduced in a vacuum. The residue was purified by silica gel chromatography with CH_2Cl_2/petrol ether (1:2) as eluant to afford a white solid (290 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30 (s, 2H), 6.81 (t, 1H), 4.70 (s, 4H), 4.59 (t, 2H), 3.62 (t, 2H), 2.56 ppm (t, 2H); ^{13}C NMR: δ = 165.5, 158.7, 131.7, 109.2, 107.8, 78.1, 76.3, 64.6, 56.3, 28.8 ppm; MS (EI): *m/z* (%) calcd for $C_{15}H_{13}BrO_4$: 337.2; found: 337.1; elemental analysis: calcd (%) for $C_{15}H_{13}BrO_4$: C 53.43, H 3.89; found: C 53.76, H 3.93.

13: A solution of **12** (33.7 mg, 0.1 mmol) and **6** (85 mg, 0.22 mmol) in THF was stirred under N_2 atmosphere. Then, a small amount of sodium ascorbate and $CuSO_4$ were added to the solution. The resulting solution was then stirred at RT for 10 h. After evaporation of the solvents, the crude product was then purified by silica gel chromatography (CH_2Cl_2 to CH_2Cl_2/MeOH = 30:1) to afford a brown solid (130 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61 (s, 2H), 7.49 (m, 6H), 7.32 (s, 2H), 7.22 (s, 1H), 7.14 (m, 5H), 6.92 (d, 4H), 6.86 (s, 1H), 6.75 (d, 4H), 6.56 (s, 2H), 5.95 (s, 2H), 5.19 (s, 4H), 4.60 (m, 6H), 4.0 (t, 4H), 3.62 (t, 2H), 3.01 (s, 12H), 2.57 (s, 6H), 2.42 (t, 4H), 1.44 (s, 6H), 1.34 ppm (s, 6H); ^{13}C NMR: δ = 165.6, 159.5, 159.0, 154.3, 153.1, 151.6, 143.5, 142.9, 141.1, 138.9, 137.4, 134.2, 132.1, 131.9, 129.9, 129.4, 128.0, 123.5, 120.6, 116.8, 115.0, 112.2, 108.9, 106.7, 64.6, 64.4, 62.4, 47.4, 40.4, 30.2, 28.9, 15.05, 14.7 ppm; MS (MALDI): *m/z* (%) calcd for $C_{77}H_{79}B_2BrF_4N_{12}O_6$: 1444.6; found: 1444.8; elemental analysis: calcd (%) for $C_{77}H_{79}B_2BrF_4N_{12}O_6$: C 63.96, H 5.51, N 11.62; found: C 63.62, H 5.13, N 11.22.

14: Dry DMF (10 mL) was added to a 25 mL-capacity flask containing **13** (145 mg, 0.1 mmol) and sodium azide (32.5 mg, 0.5 mmol). The mixture was stirred at RT for 4 h before being cooled. After the reaction was completed, the mixture was poured into water (50 mL), then extracted with $CHCl_3$ several times. The combined organic phase was dried over Na_2SO_4, and the solvent was removed under vacuum. The crude residue was purified by silica gel chromatography with (CH_2Cl_2 to CH_2Cl_2/MeOH = 30:1) as eluant, to afford a brown solid (127 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60 (s, 2H), 7.47 (m, 6H), 7.32 (s, 2H), 7.21 (s, 1H), 7.11 (s, 2H), 7.09 (d, 4H), 6.91 (d, 4H), 6.78 (s, 1H), 6.65 (d, 4H), 6.55 (s, 2H), 5.93 (s, 2H), 4.57 (t, 4H), 4.46 (t, 2H), 3.98 (t, 4H), 3.56 (t, 2H), 2.99 (s, 12H), 2.56 (s, 6H), 2.16 (t, 4H), 1.42 (s, 6H), 1.33 ppm (s, 6H); ^{13}C NMR: δ = 165.8, 159.5, 159.0, 154.8, 152.9, 151.2, 143.5, 142.9, 141.0, 138.9, 137.9, 133.5, 131.6, 129.8, 129.4, 127.9, 124.7, 123.5, 120.6, 117.8, 115.1, 114.4, 112.1, 108.9, 107.6, 64.4, 64.2, 62.3, 48.5, 47.4, 40.3, 30.0, 28.9, 15.0, 14.7, 14.6 ppm; MS (MALDI): *m/z* (%) calcd for $C_{77}H_{79}B_2F_4N_{15}O_6$: 1407.6; found: 1407.8; elemental analysis: calcd (%) for $C_{77}H_{79}B_2F_4N_{15}O_6$: C 65.68, H 5.65, N 14.92; found: C 65.42, H 5.16, N 15.37.

2-Bromoethyl-3,5-bis(3,5-bis(2-propynyloxy)benzyloxy)benzoate (16): To a stirred solution of 3,5-bis(3,5-bis(2-propynyloxy)benzyloxy)benzoic acid (550 mg, 1 mmol) and 2-bromoethanol (124 mg, 1 mmol) in anhydrous CH_2Cl_2 (50 mL) cooled on an ice bath, was added 4-DMAP (25 mg, 0.2 mmol) and EDC·HCl (205 mg, 1.1 mmol), and the reaction mixture was stirred for 10 h at RT. The solution was washed with a saturated solution of citric acid and H_2O. The organic layer was dried over anhydrous $MgSO_4$ and the filtrate was reduced in vacuum. The residue was purified by silica gel chromatography with CH_2Cl_2/petrol ether (1:2) as eluant to afford a white solid (592 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28 (s, 2H), 6.83 (s, 1H), 6.77 (m, 4H), 6.56 (m, 2H), 5.00 (s, 4H), 4.66 (d, 8H), 4.59 (t, 2H), 3.61 (t, 2H), 2.53 ppm (t, 4H); ^{13}C NMR: δ = 165.8, 159.7, 159.0, 139.1, 131.7, 108.9, 107.0, 102.0, 78.5, 75.9, 70.1, 64.5, 28.9 ppm; MS (MALDI): *m/z* (%) calcd for $C_{35}H_{29}BrO_8$: 656.1 [M+Na$^+$]; found: 679.2; elemental analysis: calcd (%) for $C_{35}H_{29}BrO_8$: C 63.93, H 4.45; found: C 64.35, H 4.19,

17: A solution of **16** (65.6 mg, 0.1 mmol) and **6** (211 mg, 0.5 mmol) in THF were stirred under N_2 atmosphere. Then, a small amount of sodium ascorbate and $CuSO_4$ were added to the solution. The resulting solution was stirred at RT for 10 h. After evaporation of the solvents, the crude product was purified by silica gel chromatography (CH_2Cl_2 to CH_2Cl_2/MeOH = 20:1) to afford a brown solid (130 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57 (s, 4H), 7.45 (m, 12H), 7.19 (s, 2H), 7.14 (s, 2H), 7.08 (d, 2H), 6.89 (d, 2H), 6.78 (s, 1H), 6.67 (m, 12H), 6.53 (s, 2H), 6.50 (s, 4H), 5.92 (s, 4H), 5.11 (s, 12H), 4.99 (s, 4H), 4.54 (m, 10H), 3.95 (t, 8H), 3.59 (t, 2H), 2.99 (s, 24H), 2.55 (s, 12H), 2.35 (t, 8H), 1.41 (s, 12H), 1.33 ppm (s, 12H); ^{13}C NMR: δ = 165.7, 159.8, 159.0, 154.8, 152.9, 151.2, 143.8, 142.9, 140.9, 139.3, 138.9, 137.9, 133.5, 131.7, 129.8, 129.4, 127.9, 124.7, 123.5, 120.6, 117.8, 115.1, 114.3, 112.2, 108.8, 106.5, 101.7, 70.1, 64.5, 62.2, 47.3, 40.3, 29.8, 15.0, 14.7, 14.6 ppm; MS (MALDI): *m/z* (%) calcd for $C_{159}H_{161}B_4BrF_8N_{24}O_{12}$: 2873.2 [$M$+Na$^+$]; found: 2896.6; elemental analysis: calcd (%) for $C_{159}H_{161}B_4BrF_8N_{24}O_{12}$: C 66.42, H 5.64, N 11.69; found: C 65.89, H 5.26, N 12.14.

18: Dry DMF (10 mL) was added to a 25 mL-capacity flask containing **17** (287 mg, 0.1 mmol) and sodium azide (32.5 mg, 0.5 mmol). The mixture was stirred at RT for 4 h before being cooled. After the reaction was completed, the mixture was poured into water (50 mL), then extracted with $CHCl_3$ several times. The combined organic phase was dried over Na_2SO_4, and the solvent was removed under vacuum. The crude residue was purified by silica gel chromatography with (CH_2Cl_2 to CH_2Cl_2/MeOH = 20:1) as eluant, to afford a brown solid (227 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58 (s, 4H), 7.44 (m, 12H), 7.19 (s, 2H), 7.13 (s, 2H), 7.05 (d, 2H), 6.89 (d, 2H), 6.78 (s, 1H), 6.67 (m, 12H), 6.53 (s, 2H), 6.50 (s, 4H), 5.92 (s, 4H), 5.11 (s, 12H), 4.99 (s, 4H), 4.54 (m, 8H), 4.46 (t, 2H), 3.95 (t, 8H), 3.59 (t, 2H), 2.99 (s, 24H), 2.55 (s, 12H), 2.35 (t, 8H), 1.41 (s, 12H), 1.33 ppm (s, 12H); ^{13}C NMR: δ = 165.7, 159.8, 159.3, 154.5, 152.9, 151.2, 143.6, 143.0, 141.1, 139.3, 139.1, 137.9, 133.5, 131.7, 129.6, 129.4, 128.2, 124.7, 123.5, 120.6, 117.8, 115.1, 114.3, 112.3, 108.7, 106.5, 101.7, 70.1, 64.7, 62.4, 47.1, 40.3, 29.8, 15.1, 14.6, 14.5 ppm; MS (MALDI): *m/z* (%) calcd for $C_{159}H_{161}B_4F_8N_{27}O_{12}$: 2836.2; found: 2836.8; elemental analysis: calcd (%) for $C_{159}H_{161}B_4F_8N_{27}O_{12}$: C 67.30, H 5.72, N 13.33; found: C 66.88, H 5.31, N 13.08.

1: A solution of **10** (71.4 mg, 0.1 mmol) and **4** (277 mg, 0.5 mmol) in THF were stirred under N_2 atmosphere. Then, a small amount of sodium ascorbate and $CuSO_4$ were added to the solution. The resulting solution was then stirred at RT for 2 h. After evaporation of the solvents, the

crude product was then purified by silica gel chromatography (CH_2Cl_2 to CH_2Cl_2/MeOH = 50:1) to afford a brown solid (249 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03 (t 8H), 7.65 (d, 4H), 7.44 (d, 12H), 7.13 (m, 20H), 6.88 (m, 12H), 6.63 (d, 8H), 6.48 (d, 4H), 5.93 (d, 4H), 5.24 (d, 8H), 4.59 (d, 8H), 3.97 (d, 8H), 2.99 (s, 24H), 2.55 (s, 12H), 1.40 ppm (m, 24H); ^{13}C NMR: δ = 168.3, 160.6, 159.5, 159.1, 157.7, 154.9, 152.9, 151.2, 145.3, 144.0, 143.8, 143.0, 142.6, 140.9, 138.9, 138.0, 133.6, 132.2, 131.7, 131.3, 131.0, 129.9, 129.4, 129.1, 128.0, 126.0, 124.9, 123.6, 120.6, 117.9, 115.1, 112.2, 64.5, 64.4, 62.2, 52.8, 47.4, 40.4, 30.0, 15.1, 14.7 ppm; MS (MALDI): *m*/*z* (%) calcd for $C_{168}H_{162}B_5F_{10}N_{27}O_8$: 2931.3; found: 2932.5; elemental analysis: calcd (%) for $C_{168}H_{162}B_5F_{10}N_{27}O_8$: C 68.84, H 5.57, N 12.9; found: C 68.48, H 5.13, N 13.42.

2: A solution of **10** (7.14 mg, 0.01 mmol) and **14** (70 mg, 0.05 mmol) in THF were stirred under N_2 atmosphere. Then, a small amount of sodium ascorbate and $CuSO_4$ were added to the solution. The resulting solution was stirred at RT for 5 h. After evaporation of the solvents, the crude product was then purified by silica gel chromatography (CH_2Cl_2 to CH_2Cl_2/MeOH = 10:1) to afford a brown solid (51.4 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.02 (t, 8H), 7.74 (d, 8H), 7.65 (m, 12H), 7.46 (m, 24H), 7.03 (m, 38H), 6.83 (m, 24H), 6.66 (d, 8H), 6.53 (d, 8H), 5.90 (d, 8H), 5.18 (d, 8H), 4.81 (t, 16H), 4.53 (m, 16H), 4.24 (t, 8H), 3.95 (m, 16H), 2.98 (s, 24H), 2.60 (s, 12H), 1.40 ppm (m, 24H); ^{13}C NMR: δ = 168.5, 165.2, 161.3, 160.8, 159.3, 156.8, 154.5, 153.7, 152.2, 150.1, 145.8, 145.0, 144.2, 143.4, 143.0, 141.8, 141.2, 139.8., 138.5, 135.7, 133.0, 132.2, 130.7, 131.3, 131.1, 130.5, 129.6, 129.0, 128.6, 126.4, 124.7, 124.1, 120.5, 118.3, 114.5, 111.0, 64.8, 64.6, 62.3, 50.5, 44.9, 38.8, 28.6, 15.0, 14.8 ppm; MS (MALDI): *m*/*z* (%) calcd for $C_{352}H_{346}B_9F_{18}N_{63}O_{28}$: 6343.8 [$M$+$Na^+$]; found: 6366.4; elemental analysis: calcd (%) for $C_{352}H_{346}B_9F_{18}N_{63}O_{28}$: C 66.62, H 5.50, N 13.9; found: C 66.87, H 5.24, N 13.61.

3: A solution of **10** (7.14 mg, 0.01 mmol) and **14** (142 mg, 0.05 mmol) in THF were stirred under N_2 atmosphere. Then, a small amount of sodium ascorbate and $CuSO_4$ were added to the solution. The resulting solution was then stirred at RT for 10 h. After evaporation of the solvents, the crude product was then purified by silica gel chromatography (CH_2Cl_2 to CH_2Cl_2/MeOH = 5:1) to afford a brown solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.08 (t, 8H), 7.75 (d, 8H), 7.61 (m, 24H), 7.42 (m, 48H), 7.05 (m, 76H), 6.88 (m, 48H), 6.52 (d, 8H), 6.32 (d, 16H), 5.90 (s, 16H), 5.21 (d, 8H), 4.93 (m, 32H), 4.55 (m, 32H), 4.32 (t, 8H), 4.15 (s, 16H), 3.92 (m, 32H), 3.55 (t, 8H), 2.98 (s, 24H), 2.55 (s, 12H), 1.35 ppm (d, 24H); ^{13}C NMR: δ = 169.1, 165.4, 161.7, 158.6, 158.2, 156.7, 155.4, 154.3, 153.1, 152.7, 151.6, 149.2, 146.8, 146.5, 145.1, 144.7, 143.9, 143.6, 143.1, 142.8, 141.9, 140.6, 139.3, 138.7, 138.3, 135.9, 133.2, 132.6, 132.0, 131.6, 131.2, 130.4, 129.7, 129.0, 128.4, 127.6, 126.5, 125.1, 122.4, 118.6, 117.2, 116.7, 113.8, 112.7, 108.7, 67.5, 66.8, 63.6, 54.5, 48.4, 46.4, 32.2, 15.7, 15.2 ppm; elemental analysis: calcd (%) for $C_{680}H_{674}B_{17}F_{34}N_{111}O_{52}$ (12058.5): C 67.7, H 5.63, N 12.89; found: C 67.11, H 5.21, N 13.44.

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